CHAPTER 4

CHARACTERIZATION OF NANOMATERIALS

LEARNING OBJECTIVES

- Introduction, X-ray diffraction, Optical microscopy, Scanning electron microscopy
- Transmission electron microscopy, Atomic force microscopy, Sanning tunneling microscopy.

4.0 INTRODUCTION

Characterization of nanomaterials is an important step to understand and control of synthesis of nanomaterials and their applications. The fabrication and characterization of nanomaterials have been a great challenge for scientists and researchers because of numerous applications of differnet types of nanomaterials. The individual nanoparticles cannot be viewed by the human eyes, because of their small size which is of the order of $\frac{1}{100}$ th part of the wavelength of light. They can be viewed by light. They can be viewed by high resolution optical microscopes only in liquid samples of nanomaterials under certain conditions. Therefore some specialized techniques are required to view the nanoparticles and these techniques are known as characterization techniques. These techniques are useful to know the particle size distribution in the material, surface morphology, interface valume ratio, band structure, lattice constants etc.

Nanoparticle characterization can be done by using a variety of techniques. These techniques can be classified ino two categories namely direct detection techniques and indirect detection techniques. Direct detection techniques include scanning electron microscopy (SEM), transmission electron microscopy, (TEM), atomic force microscopy (AFM) and Scanning tunneling microscopy (TEM). These characterization techniques can image nanoparticles, directly measure sizes, particle distribution, surface morphology and interface information. These techniques are effective to obtain basic information about nanoparticles. Indirect detection techniques includes X-ray diffraction (XRD) and neutron scattering (NS). X-ray diffraction technique is useful to know the crystal structure and lattice constant of the nanoparticles. Neutron scattering technique is helpful to reveal the photon modes of the materials.

4.1. X-RAY DIFFRACTION

X-Ray Diffraction (XRD) technique is an important tool for the study of crystal structures and atomic spacing. XRD is based on constructive interference of monochromatic X-rays on a crystalline sample. The schematic diagram of a X-ray diffraction system is shown in the fig 4.1 (a).

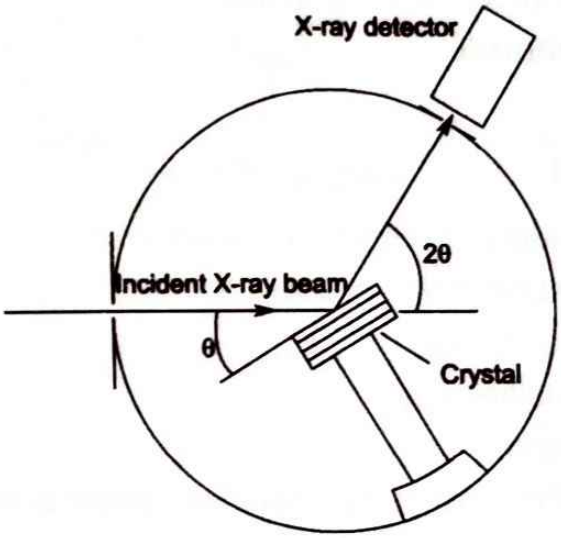

Fig.4.1(a) Schematic of X-Ray diffraction system

The X-rays are produced by a cathode ray tube and filtered to produce monochromatic X-rays. These monochromatic X-rays are collimated to concentrate and directed towards the crystalline sample. The crystalline sample acts as a three dimensional diffraction grating for X-ray wavelengths similar to the spacing of planes in a crystal lattice. The interaction of the incident X-rays with the crystalline sample produces constructive interference if the conditions of Bragg's law i.e., $2d \sin\theta = n\lambda$ are satisfied. This law relates the wavelength of electromangetic radiation (λ) to the diffraction angle (θ) and the lattice spacing (d) in a crystalline sample. These diffraced X-rays are then detected, processed and computed. All possible diffraction directions of the crystal lattice can be attained by scanning the sample through a range of angles 2θ. The crystal can be identified by the conversion of the diffraction peaks to d-spacings because each type of crystal has a set of unique spacings. The analysis of crystalline samples, semi-crystalline samples and amorphous samples at nano-scale can be done using X-ray diffraction technique. Dimensions and sizes of crystallite are the fundamental characteristics of nanomaterials and are useful to understand and control the bulk properties. Small crystallite size produces broadened diffraction. patterns. The information about crystalline size and other aspects such as lattice distortions due to composition or micro strain variations and faulting can be obtained from the analysis of peak shapes.

X-Ray diffraction provides an adaptable technique for measuring crystalline phases, degrees of crystallinity and structures of materials range from polymers to glass ceramics.

X-Ray diffraction also provides the technique for measuring crystalline orientatioin. Crystallites in a fabricated structure are oriented as a design feature or as a characteristics of the processing technology. Nano-scale orientation can affect the performance of the product. The orientation distribution of tiny nano-metre thick platelets on the surface of a polymer film can be measured by XRD technique and this indicates alignment with the film surface which can have a major effect on the surface properties of the polymer.

According to Scherrer formula

$$\beta = \frac{K\lambda}{D \cos\theta}$$

where β = Integral breadth of a reflection located at 2θ.

K = Sherrer constant (0.9)

λ = Wavelength of X-rays

D = Average crystalline size

θ = Diffraction angle

Sherrer observed that if the size of the crystalline sample is small the line is broadened. Sherrer formula relates the crystallite size to the broadening.

The X-Rays diffraction pattern of copper nanopowder is shown in the figure 4.1(b). Each peak of the diffraction pattern in assigned Miller induces (h, k, l) to index a power diffraction pattern.

4.2 OPTICAL MICROSCOPY

Optical microscopy is a technique used to closely view a sample by an optical microscope through the magification of the lenses with visible light.

An optical microscope is also known as light microscope. It consists of one or a number of lenses to magnify images of small crystalline samples with visible light. The lenses are placed between the sample and the viewer's eye to magnify the image so that the sample can be examined in details.

There are different types of optical microscopes that can vary from a very basic design to high complexity to offer high resolution and contrast. Some of the types of optical microscopes are simple microscope, compound microscope, digital microscope, stereo microscope, comparison microscope, and inverted microscope.

Simple microscope consists of a single lens to magnify the image of the sample.

Compound microscope consists of a series of lenses to magnify the image of the sample to a higher resolution.

Digital microscope consists of a single or a series of lenses and it uses a computer to visualize the image of the sample without the requirement of an eyepiece to view the image.

Stereo microscope provides a stereoscopic image of the sample which is useful for dissections.

Comparison microscope allows for the simultaneous view of two different samples, one in each eye. Inverted microscope views, the sample from underneath, which is useful to examine the liquid cell cultures. The schematic diagram of an optical microscope (simple microscope) in shown in the fig. 4.2(a)

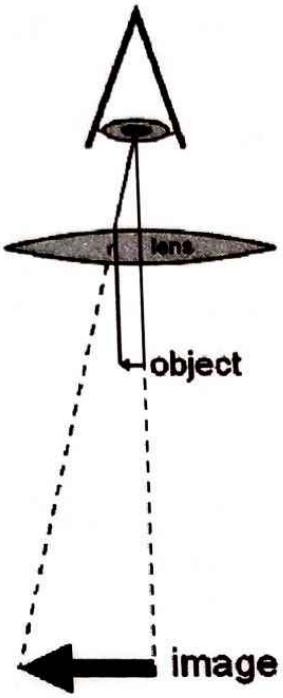

Fig. 4.2(a) : Schematic diagram of simple microscope

The schematic diagram of an optical microscope (compound microscope) is shown in the figure 4.2 (b)

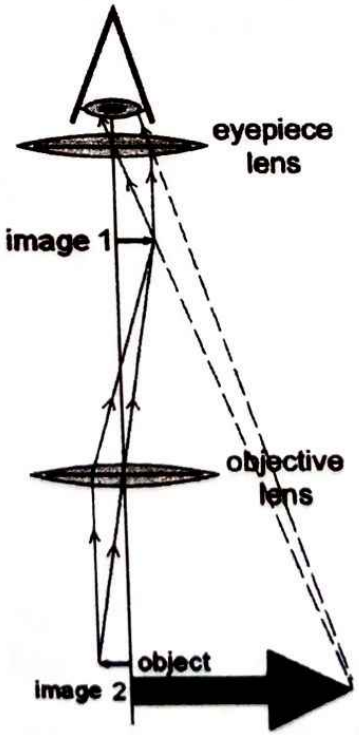

Fig. 4.2(b) : Schematic diagram of compound microscope

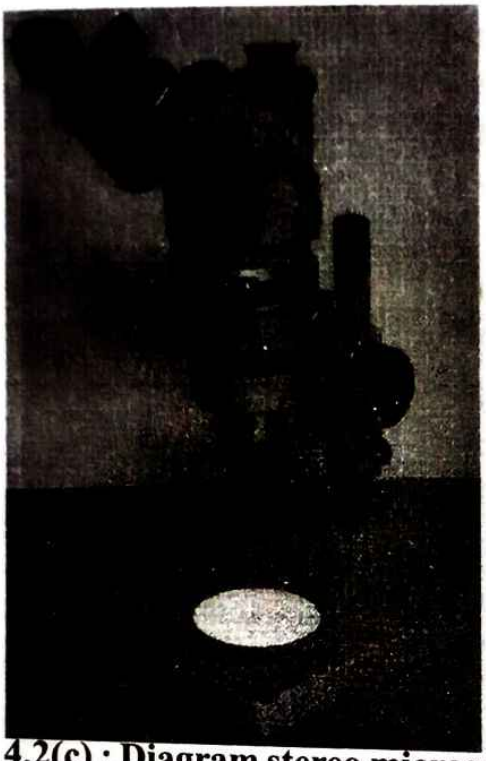

Fig. 4.2(c) : Diagram stereo microscope

The schematic diagram of a stereo microscope is shown in the fig. 4.2(c)

Fig. 4.2(d) : Diagram of comparison microscope

In a comparison microscope, two identical microscopes are connected to a single comparison eyepiece. The viewer sees the images from both microscopes next to one another, as in the inset image. The schematic diagram of a comparison microscope is shown in the fig. 4.2(d)

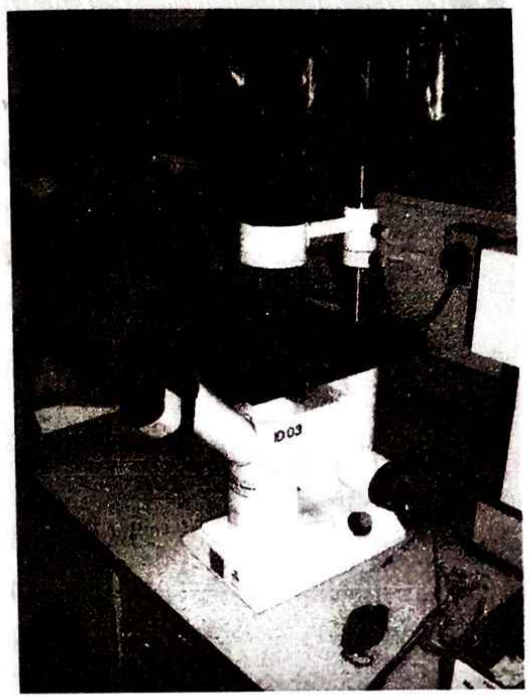

Fig. 4.2(e) : Diagram of inverted microscope

The schematic diagram of an inverted microscope is shown in the fig. 4.2(e)

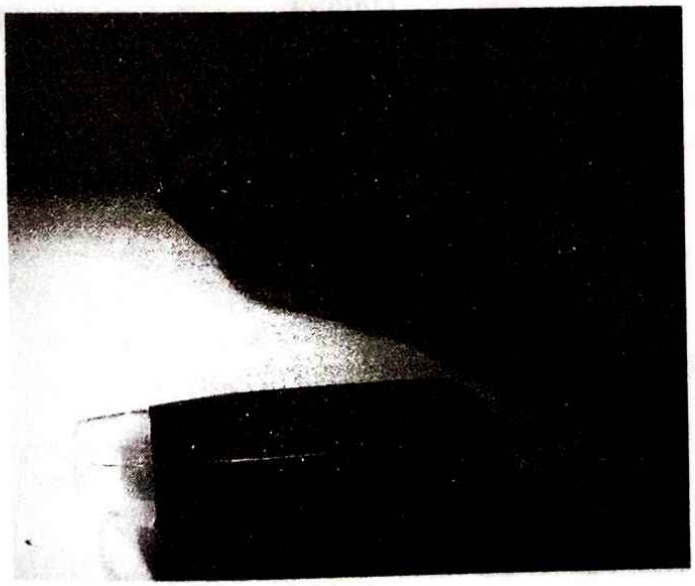

Fig. 4.2(f) : Diagram of digital microscope

The schematic diagram of a digital microscope is shown in the fig. 4.2(f)

In order to use an optical microscope effectively, it is important to ensure that the microscope is set up correctly. The objective lens of the microscope must be close to the sample to allow the light inside the tube of the microscope. This produces an enlarged and inverted image of the sample which can be viewed through the eyepiece of the microscope.

Optical microscopy is used in micro-electronics, nano-electronics and nanophysics.

Optical microscope can produce upto magnification of 1200x and resolution up to 0.25 micrometre.

Limitations :

Optical microscope has the following limitations.

(i) The resolution of an optical microscope cannot be smaller than the half of the wavelength of light.

(ii) Optical microscope has low magnification.

(iii) It produces poor surface view of the sample.

4.3 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy is a technique used to view the high resolutioin images of the surface of a sample by scanning electron microscope. In scanning electron microscope the images of the surface of a material are obtained by scanning the sample with a high energy beam of electrons. The schematic diagram of a scanning electron microscope is shown in the figure 4.3.

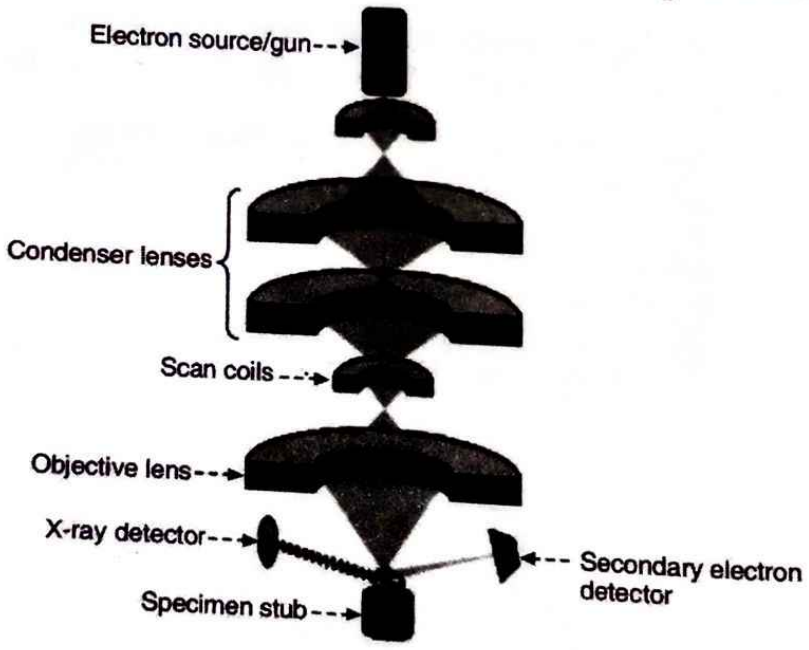

Fig. 4.3 Schematic diagram of SEM.

The whole system must be evacuated to prevent scattering of the electrons by stray air molecules and the sample must absorb or reflect electrons.

Scanning electron microscope consists of an electron gun which produces a stream of monochromatic electrons. The stream of electrons is then condensed by the first condenser lens

which is used to form the electron beam and limit the amount of curent in the beam. The second condenser lens is used to form the thin tight and coherent electron beam. A set of coils are used to scan the electron beam in a grid fashion, dwelling on points for a period of time determined by the scan speed. The objective lens focuses the scanning electron beam onto the part of the desired sample. When the electron beam strikes the sample and dwells for a few micro-second, interactions occur inside the sample and are detected by various instruments. These instruments count the number interactions and display a pixel on a cathode ray tube before the electron beam moves to the next dwell point. This process is repeated till the grid scan is completed. The entire pattern can be scanned 30 times per second. SEM images have a characteristic three dimensional appearance and these images are useful to judge the surface structure of the sample. The surface morphology related details are obtained by scanning electron microscopy with great precision for nanoparticles, thin films, nanocoatings, fractured-surfaces, polymer nanocomposites and other micro and nanostructures.

4.4 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy is a technique used to view the high resolution images of the surface of a sample by transmission electron microscope. In transmission electron microscope the images of the surface of the sample are obtained by the transmission of electron beam through the sample. The schematic diagram of a transmission electron microscope is shown in the figure 4.4.

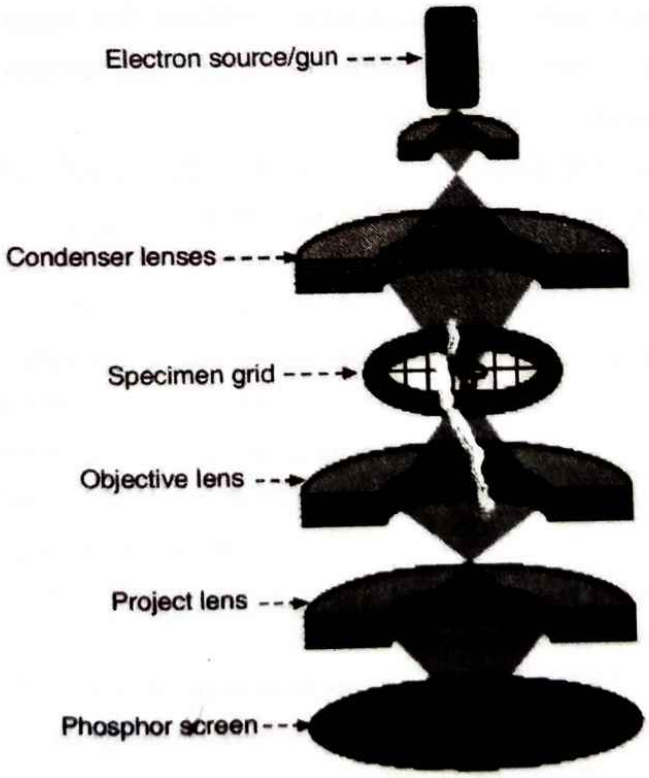

Fig. 4.4 Schematic diagram of a TEM.

The electron gun of TEM emits a high energy electron beam. This electron beam is transmitted through the sample of the material and carried the information about the inner structure of the sample. The transmitted electron beam reaches the imaging system of the TEM and the image of the sample is then magnified by a series of electromagnetic lenses till it recorded by hitting a fluorescent screen, photographic plate or light sensitive sensor or charge coupled camera. The image detected may be displayed in real time on a monitor or computer.

The working of TEM consists of the following steps. The electron gun produces a stream of monochromatic electrons, which is then focussed to a small, thin and coherent beam by the condenser lenses. The electron beam is then transmitted through the sample and the transmitted beam is focussed by the objective lens to form an image. The image is then passed through the projector lens to enlarge the image. Then the enlarged image strikes the phosphor screen and light is generated and allows the user to see the image. The lighter areas of the image represent those areas of the sample that more electrons were transmitted through and the darker areas of the image represent those areas of the sample that less electrons were transmitted through.

High resolution transmission electron microscopy (HRTEM) is an additional imaging mode in TEM, which helps to image the crystallographic structure of a sample at an atomic scale.

HRTEM is considered to be very essential to study the nanoscale properties of nanomatcricals.

Limitations : SEM has the following limitations :

(i) Extensive sample preparation is required to produce thin samples.
(ii) The struction of nanomaterials might be affected during sample preparation.
(iii) SEM is a time consumping technique.
(iv) The high energy electron beam can also damage the samples examined.
(v) It is difficult to study biological materials by SEM technique.

4.5 ATOMIC FORCE MICROSCOPY

Atomic force microscopy is a technique used to view very high resolution images of the surface of a sample by Atomic force microscope. Atomic force microscope is also known as scanning probe microscopy. Atomic force microscope has resolution of the order of fractions of a nanometer. It can obtain images with very high resolutions at any strom level. It can measure the surface roughness and texture at nanometer scale. It is a non-destsructive technique and it is used to obtain three-dimensional representation of the sampling surface with very high spatial resolution.

Atomic force microscope consists of a cantilever with sharp tip (probe) at its end which is used to scan the surface of the sample. The cantilever is made up of silicon or silicon nitride with a tip radius of curvature of the order of nanometers. When the tip is brought into the proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Forces that can be measured by AFM technique, are mechanical contact force, Vander Waals forces, capillary forces, chemical bonding, electrostatic forces,

magnetic forces, solvation forces etc. The deflection is measured by using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. The schematic diagram of an atomic force microscpe is shown in the figure 4.5.

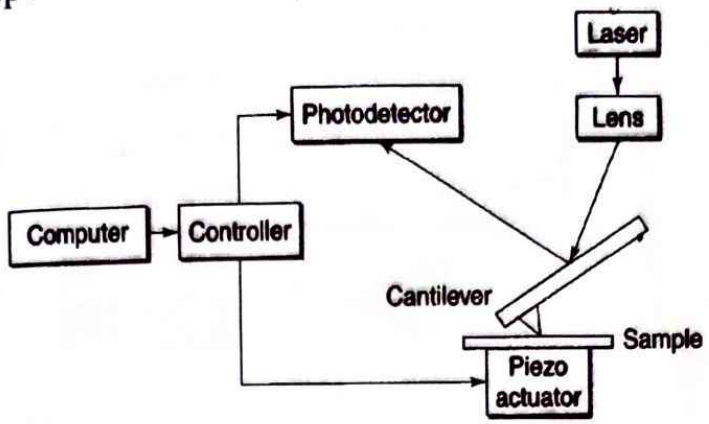

Fig. 4.5 : Schematic diagram of an atomic force microscope

The tip is scanned across the sample using piezoelectric scanners during scanning take place in the tip sample interaction. This is monitored using an optical lever detection system. The microscopic images are then generated through the feedback loop established between optical detection system and the piezoelectric scanners. There are three common scan modes in AFM. These scan modes are contact mode, non-contact mode and tapping mode. The contact mode is also known as static mode. In static mode the force between the tip and the surface is kept constant. In general scanning modes in AFM are classified as static mode and dynamic mode. Dynamic modes are classified as non-contact mode and tapping mode. In dynamc mode the cantilever is vibrated.

Advantages : AFM has the following advantages :

(i) It can be used to procure a 3D surface profile.
(ii) The samples do not require any special treatment.
(iii) It can be operated in liquid environment.
(iv) It can be used to study biological materials.

Limitations : AFM has the following limitations :

(i) The scanning rate of an AFM is very slow.
(ii) The tip plays an important role to determine the resolution of the image.
(iii) The image size scanned in AFM is very low.

4.6 SANNING TUNNELING MICROSCOPY

STM is a technique used to view the images of the surface of a sample at the atomic level by scanning tunnelling microscope.

STM was invented by Gerd Binnig and Heinrich Rohrer in 1881. STM is a position sensitive device which produces resolution of the order of 0.1 nanometre lateral and 0.01 nanometre depth resolutions. STM can be used in ultra-high vacuum, air, water, liquids and gas and at temperatures ranging from 0K to few hundred kelvin.

The schematic diagram of a scanning tunnelling microscope is shown in the figure-4.6.

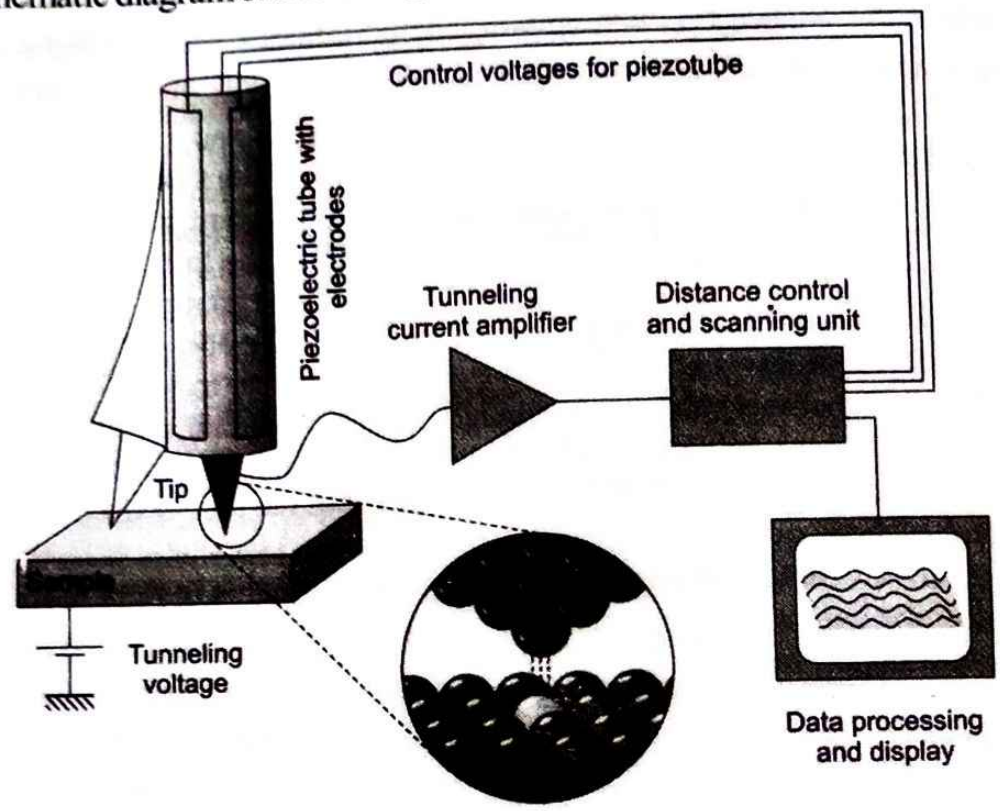

Fig. 4.6 : Schematic diagram of a scanning microscope

STM is based on the principle of quantum tunnelling. When a conducting narrow tip is brought nearer to the surface to be analyzed, a potential difference applied between two terminals can allow electrons to tunnel through the vacuum between them. The resulting tunnelling current is a function of tip position, applied voltage and the local density of states of the surface of sample material. Information regarding the surface morphology can be acquired by monitoring the current as the tip position scans across the surface and is generally displaced in an image form. It is a challanging technique because it requires extremely clean and stable surfaces, sharp tips, excellent vibration control and sophisticated electrons for the accuracy.

Initially a potential difference is applied and the tip in brought near the sample surface by some coarse sample-to-tip control, which is turned off when the tip and sample are close to each other. At close range, fine control of the tip near the sample, maintaining tip-sample separation W in the range of 4 - 7 Å which is the equilibrium position between attractive $3 < W < 10$Å and repulsive $W < 3$A interactions. In this condition the potential difference will cause electrons to tunnel between the tip and the sample creating a current that can be measured. Once tunnelling is established the tip's bias and the position with respect to the sample can be varied and the data are obtained from the resulting changes in current.

If the tip is moved across the sample in the XY-plane the changes in surface height and density of states cause changes in tip current. These changes are mapped in images to present the

surface morphology. The change in current with respect to position tip can be measured at constant height (z) or the height (z) corresponding to a constant current can be measured. These two modes are called constant height mode and constant current mode respectively. In constant current mode the feedback electronic system adjusts the height by passing a voltage to the piezoelectric height control mechanism. This causes a height variation and hence the image comes from the tip topography across the sample and gives a constant charge density. In constant height mode the voltage and height are both held constant while the current changes. This causes an image mode of current changes over the surface, which can be related to charge density on the surface. The advantage of using constant height mode is that it is faster than the constant current mode because the piezoelectric movements require more time to resister the height change at constant current mode than the current changes at constant height mode. All images obtained by STM are grey-scale, with colour optionally added in post-processing in order to visually emphasize on important features.

STM can also be used to obtain information on the electronic structure at a given location of the sample that can be obtained by sweeping voltage and measuring current at a specific location. STM has the ability to make extremely local measurements such as the density of states of an impurity site can be compared to the density of states far from the impurities.

STM consists of a scanning tip, piezoelectric controlled height and surface (x, y) scanner, course sample-to-tip control, vibration isolation system and a computer. The resolution of an image produced by STM depends on the radius of curvature of the scanning tip. Image artifacts may occur if the scanning tip has more than one tip at the end. This leads to double-tip imaging that in a situation on which both the tips contribute to the tunneling. Hence it is essential to develop processes to obtain a sharp tip. In recent years carbon nanotube (CNT) has been used for this purpose. The scanning tip is also made of tungsten, platinum-iridium and gold. Tungsten tips are usually made by electrochemical etching and platinum-iridium tips are made by mechanical shearing.

Due to extreme sensitivity of tunnel current to height, proper vibration isolation or an extremely rigid STM body is essential to obtain usual results. In the first STM invented by Binning and Rohrer, magnetic levitation was used to keep the STM free from vibrations. Recently mechanic spring or gas spring systems are used to keep the STM vibration free. In addition to this mechanisms to reduce the eddy currents are also implemented. The scanning tip position with respect to the sample, scanning of the sample and acquiring the data are controlled by the computer. The computer can also be used to enhance the image by the help of image processing and to perform quantitative measurements.

SUMMARY

- Direct detection techniques include scanning electron microscopy (SEM), transmission electron microscopy, (TEM), atomic force microscopy (AFM) and Scanning tunneling microscopy (TEM).
- Indirect detection techniques includes X-ray diffraction (XRD) and neutron scattering (NS).
- X-ray diffraction technique is useful to know the crystal structure and lattice constant of the nanoparticles.
- Neutron scattering technique is helpful to reveal the photon modes of the materials.
- XRD is based on constructive interference of monochromatic X-rays on a crystalline sample.
- X-Ray diffraction provides an adaptable technique for measuring crystalline phases, degrees of crystallinity and structures of materials range from polymers to glass ceramics.
- X-Ray diffraction also provides the technique for measuring crystalline orientatioin.
- According to Scherrer formula $\beta = \frac{K\lambda}{D\cos\theta}$
- Optical microscopy is a technique used to closely view a sample by an optical microscope through the magification of the lenses with visible light.
- An optical microscope is also known as light microscope.
- Simple microscope consists of a single lens to magnify the image of the sample.
- Compound microscope consists of a series of lenses to magnify the image of the sample to a higher resolution.
- Digital microscope consists of a single or a series of lenses and it uses a computer to visualize the image of the sample without the requirement of an eyepiece to view the image.
- Stereo microscope provides a stereoscopic image of the sample which is useful for dissections.
- Comparison microscope allows for the simultaneous view of two different samples, one in each eye.
- Inverted microscope views, the sample from underneath, which is useful to examine the liquid cell cultures.
- Optical microscopy is used in micro-electronics, nano-electronics and nanophysics.
- The resolution of an optical microscope cannot be smaller than the half of the wavelength of light.
- Optical microscope has low magnification.Scanning electron microscopy is a technique used to view the high resolutioin images of the surface of a sample by scanning electron microscope.
- In scanning electron microscope the images of the surface of a material are obtained by scanning the sample with a high energy beam of electrons.

- The surface morphology related details are obtained by scanning electron microscopy with great precision for nanoparticles, thin films, nanocoatings, fractured-surfaces, polymer nanocomposites and other micro and nanostructures.
- Transmission electron microscopy is a technique used to view the high resolution images of the surface of a sample by scanning electron microscope.
- In transmission electron microscope the images of the surface of the sample are obtained by the transmission of electron beam through the sample.
- High resolution transmission electron microscopy (HRTEM) is an additional imaging mode in TEM, which helps to image the crystallographic structure of a sample at an atomic scale.
- HRTEM is considered to be very essential to study the nanoscale properties of nanomatcricals.
- SEM is a time consumping technique.
- SEM is difficult to study biological materials by SEM technique.
- Atomic force microscopy is a technique used to view very high resolution images of the surface of a sample by Atomic force microscope.
- Atomic force microscope is also known as scanning probe microscopy.
- Atomic force microscope has resolution of the order of fractions of a nanometer.
- The scanning rate of an AFM is very slow.
- The image size scanned in AFM is very low.
- STM is a technique used to view the images of the surface of a sample at the atomic level by scanning tunnelling microscope.
- STM can be used in ultra-high vacuum, air, water, liquids and gas and at temperatures ranging from 0K to few hundred kelvin.
- STM is based on the principle of quantum tunnelling.
- All images obtained by STM are grey-scale, with colour optionally added in post-processing in order to visually emphasize on important features.
- STM can also be used to obtain information on the electronic structure at a given location of the sample that can be obtained by sweeping voltage and measuring current at a specific location.
- STM has the ability to make extremely local measurements such as the density of states of an impurity site can be compared to the density of states far from the impurities.

QUESTIONS

Long Answer Type Questions :

1. Describe X-Ray diffraction technique for the characterization of nanoparticles.
2. Describe the basic working principle of optical microscope.
3. Describe scanning electron microscopy technique for characterization of nanoparticles.

4. Describe transmission electron microscopy technique for the characterization of nanoparticles.
5. Describe the working principle of atomic force microscopy.
6. Describe the working principle of scanning tunneling microscopy.

Very Short Answer Type Questions :

1. Which technique is an important tool for the study of crystal structures and atomic spacing ?
2. Which technique is helpful to reveal the photon modes of the materials ?
3. Write Sherrer formula.
4. What are direct detection techniques ?
5. What are indirect detection techniques ?
6. State and explain Bragg's law.
7. Which technique is used to closely view a sample through the magnification of the lenses with visible light ?
8. What is compound microscope ?
9. What is digital microscope ?
10. What is stereo microscope ?
11. What is comparison microscope ?
12. What is optical microscopy ?
13. What is inverted microscope ?
14. Which microscope produces poor surface view of the sample ?
15. Which technique is used to view the high resolution images of the surface of a sample by an electron microscope ?
16. Which technique is used obtain the surface morphology related details with great precision for nano-particles, thin films, nano-coatings, fractured surfaces, polymer nano-composites and other micro and nano-structures ?
17. What is transmission electron microscopy ?
18. What is HRTEM ?
19. What is atomic force microscopy ?
20. What is scanning probe microscopy ?
21. What is scanning tunneling microscopy ?
22. Which technique is used to view the images of the surface of a sample at the atomic level ?

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